STATISTICAL MECHANICS

(NEP Semester IV - Chapter 4)

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❖ *What is Statistical Mechanics?*

- Microstate
- Macrostate
- Partition Function
- The idea of interaction

  (a) particle (system) - external environment

  (b) particle (within a system of many particles)
- Entropy : Disorder Number
- Equipartition Theorem : the energies are distributed equally in different degrees of freedom.
- Temperature
- Distributions : Maxwell-Boltzmann, Fermi-Dirac, Bose-Einstein

Why do we study Statistical Mechanics?

- We apply statistical mechanics to solve for real systems (a system for many particles).

- We can easily solve the Schrodinger's equation for 1 particle / atom / molecule.

DEFINITIONS:-

❖ Microstate:

A Microstate is defined as a state of the system where all the parameters of the constituents (particles) are specified.

Many microstates exist for each state of the system specified in macroscopic variables (E, V, N, ...) and there are many parameters for each state. We have 2 perspectives to approach in looking at a microstate :

DEFINITIONS:-

- **Classical Mechanics:-**

The position (x,y,z) and momentum (Px, Py, Pz) will give 6N degrees of freedom and this is put in a phase space representation.

- **Quantum Mechanics:-**

The energy levels and the state of particles in terms of quantum numbers are used to specify the parameters of a microstate.

MACROSTATE

- ✓ A Macro-state is defined as a state of the system where the distribution of particles over the energy levels is specified.

- ✓The macro-state includes what are the different energy levels and the number of particles having particular energies. It contains many microstates.

MACROSTATE

✓In the equilibrium thermodynamic state, we only need to specify 3 macroscopic variables (P,V,T) or (P,V,N) or (E,V,N), where P : pressure, V : Volume, T : Temperature, **N** : Number of particles and E : Energy. The equation of state for the system relates the 3 variables to a fourth, for e.g. for an ideal gas.

$$PV = nRT$$

✓ We also have examples of other systems like magnetic systems (where we include M, the magnetization). However, the equilibrium macrostate is unknown from thermodynamics.

MICROSTATES

- The total number of microstates is:

$$\Omega = \sum w$$

$$\text{True probability } P(n) = \frac{w_n}{\Omega}$$

- For a very large number of particles

$$\Omega \cong w_{max}$$

PROBABILITY

An event (very loosely defined) – any possible outcome of some measurement.

An event is a statistical (random) quantity if the probability of its occurrence, ***P***, in the process of measurement is < 1.

The "sum" of two events: in the process of measurement, we observe either one of the events.

Addition rule for independent events: $P\,(i \text{ or } j) = P\,(i) + P\,(j)$

(independent events – one event does not change the probability for the occurrence of the other).

The "product" of two events: in the process of measurement, we observe both events.

Multiplication rule for independent events: $P\,(i \text{ and } j) = P\,(i) \times P\,(j)$

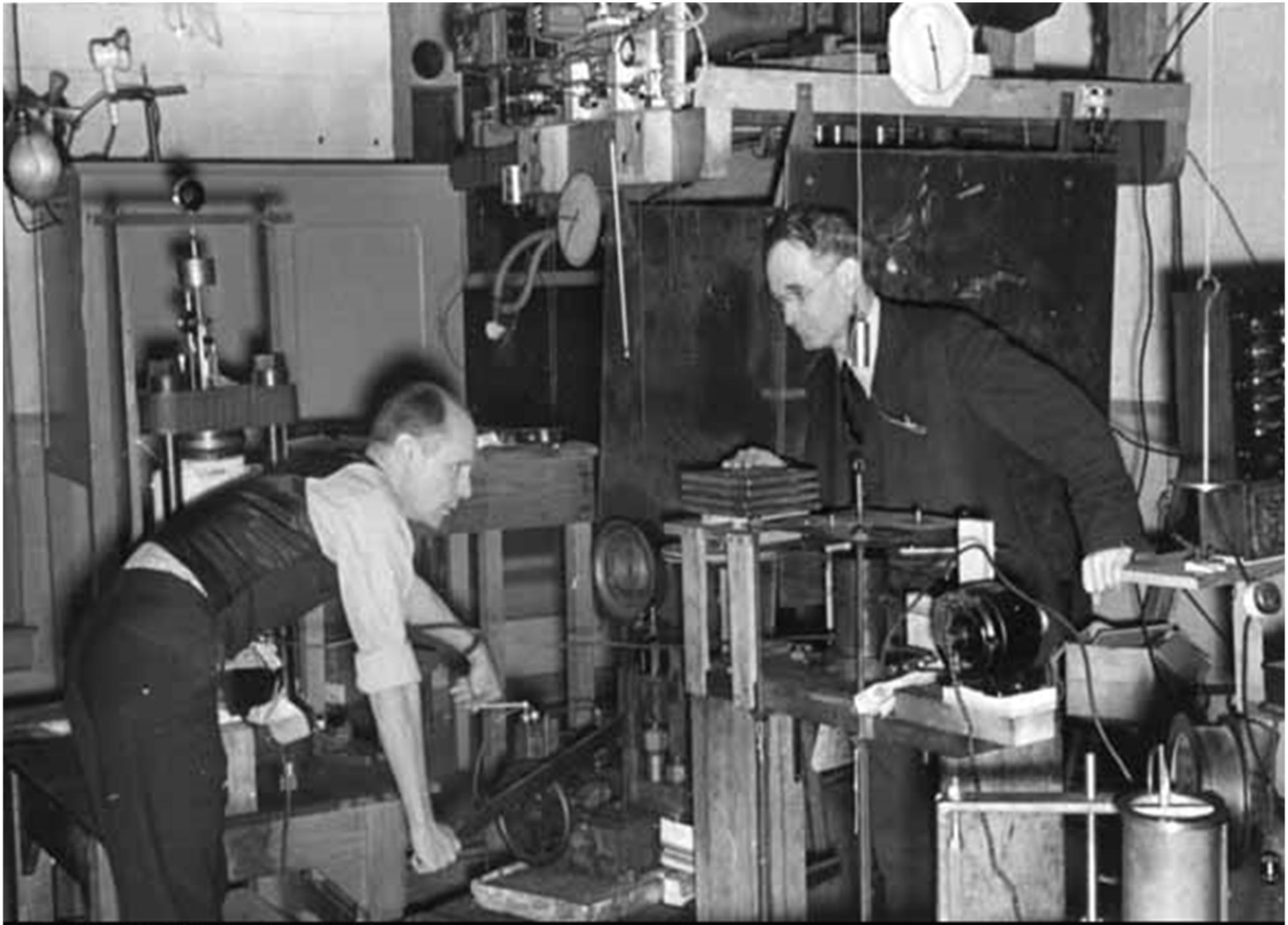
THERMODYNAMIC PROBABILITY

The term with all the factorials in the previous equation is the number of microstates that will lead to the particular macrostate. It is called the "thermodynamic probability", w_n.

$$w_n = \frac{N!}{n!(N-n)!}$$

Boltzmann Statistical Distribution

- **1877,L. Boltzmann**
- derived the distribution function when studying the collisions of gas molecules owing to which the distribution set in.
- In the thermodynamic system which is made up with classical particles, if these particles have the same mechanical properties, and they are independent, the system's most probable distribution is called **Boltzmann's statistical Distribution**.



The Boltzmann Distribution

The Austrian physicist Boltzmann asked the following question: in an assembly of atoms, what is the probability that an atom has **total energy** between **E** and **E+dE**?

His answer:

$$\Pr(E) \propto f_B(E)$$

where $$f_B(E) = Ae^{-E/kT}$$

Ludwig Boltzmann
1844 - 1906

The Boltzmann Distribution

$$f_B(E) = Ae^{-E/kT}$$

is called the **Boltzmann distribution**, $e^{-E/kT}$ is the Boltzmann factor and

$$k = 8.617 \times 10^{-5} \text{ eV/K}$$

is the **Boltzmann constant**

The Boltzmann distribution applies to **identical**, but **distinguishable** particles

Ludwig Boltzmann
1844 - 1906

The Boltzmann Distribution

The number of particles with energy **E** is given by

$$n(E) = g(E) f_B(E) = A g(E) e^{-E/kT}$$

where **g(E)** is the **statistical weight**, i.e., the number of states with energy **E**.

However, in classical physics the energy is continuous so we must replace **g(E)** by **g(E)dE**, which is the number of states with energy between **E** and **E** + **dE**. **g(E)** is then referred to as the **density of states**.

Maxwell-Boltzmann Statistics

We take another step back in time from quantum mechanics (1930's) to statistical mechanics (late 1800's).

Classical particles which are identical but far enough apart to be distinguishable obey Maxwell-Boltzmann statistics.

classical ⇔ "slow," wave functions don't overlap

distinguishable ⇔ you would know if two particles changed places (you could put your finger on one and follow it as it moves about)

Two particles can be considered distinguishable if their separation is large compared to their de Broglie wavelength.

Example: ideal gas molecules.

Maxwell-Boltzmann distribution function is

$$f(\varepsilon) = A\,e^{-\varepsilon/kT}$$

➢The number of particles having energy ε at temperature T is

$$n(\varepsilon) = A\,g(\varepsilon)\,e^{-\varepsilon/kT}\,.$$

➢ A is like a normalization constant; we integrate n(ε) over all energies to get N, the total number of particles. A is fixed to give the "right" answer for the number of particles. For some calculations, we may not care exactly what the value of A is.

- ε is the particle energy, k is Boltzmann's constant ($k = 1.38 \times 10^{-23}$ J/K), and T is the temperature in Kelvin.

- Often k is written k_B. When k and T appear together, you can be sure that k is Boltzmann's constant.

$$n(\varepsilon) = A\, g(\varepsilon)\, e^{-\varepsilon/kT}$$

We still need g(ε), the number of states having energy ε. We will find that g(ε) depends on the problem under study.

Summary

- Statistical physics is the study of the collective behavior of large assemblies of particles

- Ludwig Boltzmann derived the following energy distribution for identical, but **distinguishable**, particles $$f_B(E) = Ae^{-E/kT}$$

- The Maxwell distribution of molecular speeds is a famous application of Boltzmann's general formula